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^{1}H Spin-Lattice Relaxation in a NH_4HSO_4 Single Crystal

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The proton NMR line width and spin-lattice relaxation times for the NH_4HSO_4 single crystal were studied over a wide temperature range. The proton spin-lattice relaxation time for NH_4HSO_4 has a minimum value, which is attributed to the effect of molecular motion. The ^{1}H spin-lattice relaxation times occurring in phases I and III are attributed to the same motions of NH_4 ions. The activation energies for the reorientation motions in phases I and III are 0.98 and 4.61 kcal/mol, respectively. In phase II, the activation energy is 5.92 kcal/mol. The large change in the activation energy between phases I and II indicates that the NH_4 groups are affected during this transition; however, the motion of the NH_4^+ ions between phases II and III does not play an important role in the phase change.

KEYWORDS: ferroelectrics, crystal growth, nuclear magnetic resonance
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1. Introduction

The hydrogen sulphate family, $MHSO_4$ (M=Na, K, Rb, Cs and NH_4), has received much attention owing to its interesting properties.[1–3)] The NH_4HSO_4 crystal undergoes two phase transitions, one at $T_c = 270$ K and the other at $T_c = 160$ K, and is ferroelectric in the temperature range between 160 K and 270 K.[4–6)] It is believed that N–H···O bonds play an important role in the dielectric behavior of this crystal. The transition at $T_c = 270$ K exhibits properties typical of a phase transition of the second-order.[7)] The crystal under study undergoes a transition of the first-order at $T_c = 160$ K.[8)] Kondo *et al.*[9,10)] later reported that this crystal was ferroelastic in the room-temperature phase.

The NH_4HSO_4 crystal has been the subject of several experiments, including Raman scattering,[11)] infrared absorption,[12)] nuclear magnetic resonance (NMR),[13)] and neutron inelastic scattering.[14)] General agreement exists that the internal vibrations of the NH_4^+ ions do not change when passing through the upper transition, though the lower transition may be associated with an ordering of these ions. Both transitions appear to be accompanied chiefly by a change in the character of hydrogen bonding in the structure. The internal vibrations of the SO_4^{2-} ions are reported to showed no change at either transition.[11,12)] The results of Rush and Taylor[14)] suggest that the rotational freedom of the NH_4^+ ion is quite high. Miller *et al.*[13)] reported on the ^{1}H spin-lattice relaxation time, and based on their results, a new phase transition was proposed at 173 K, to replace the one previously reported at 160 K; they observed a striking change in the ^{1}H spin-lattice relaxation time at 173 K. In this paper, we classify NH_4HSO_4 single crystals into three phases (I, II, and III) separated by two transition temperatures.

Information regarding the structure and the internal motion of solids can be obtained from nuclear magnetic resonance techniques. From relaxation time measurements, it was determined that in the neighborhood of the phase transition temperature the slope of the relaxation time plotted as a function of temperature underwent an abrupt change. From this information, it was concluded that a change in NH_4^+ motion accompanied and reflected the phase transition.[15)] Thus, studies of the spin-lattice relaxation time were performed to determine more about the rates of motion. This study examines the line width and spin-lattice relaxation time, T_1, for ^{1}H in a NH_4HSO_4 single crystal grown by using the slow evaporation method. Our main intent was to obtain quantitative activation parameters for the types of motion that govern the relaxation and to relate them to the phase transition. Based on ^{1}H NMR data, we strove, in particular, to explain for the first time the role of NH_4^+ in the mechanism of the phase transitions.

2. Crystal Structure

X-ray examination indicates the true symmetry of the crystal at room temperature to be monoclinic, pseudo-orthorhombic. The symmetry of the pseudo-orthorhombic cell is $B2_1/a$ with $a = 24.90$ Å, $b = 4.54$ Å, $c = 14.90$ Å, and $\beta = 90.18°$, and $Z = 16$. The conventional designation for this symmetry is $P2_1/c$ with $a = 14.51$ Å, $b = 4.54$ Å, $c = 14.90$ Å, and $\beta = 120.18°$, and $Z = 8$. The c-axis is the same for both cells.[4,16,17)] In the room-temperature phase, the ammonium groups $NH_4(1)$ and $NH_4(2)$ and the sulfate groups $SO_4(1)$ and $SO_4(2)$ are inequivalent as shown in Fig. 1. Nevertheless, the symmetrically inequivalent ammo-

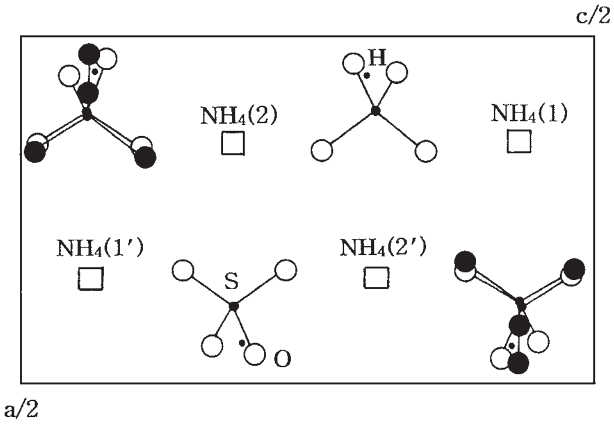

Fig. 1. Crystal structure of NH_4HSO_4 in the room temperature phase projected onto (010).

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*Corresponding author. E-mail: aeranlim@hanmail.net nium ions are in very similar asymmetric environments. The symmetry of the intermediate, ferroelectric phase is *Pc* with the twofold screw axis disappearing at the phase transition temperature. Lattice constants then become $a = 14.26$ Å, $b = 4.62$ Å, $c = 14.80$ Å, and $\beta = 121.18°$ at 243 K. Below 154 K, the symmetry is triclinic. Observations at 133 K show space group P_1 with $a = 14.24$ Å, $b = 4.56$ Å, $c = 15.15$ Å, and $\beta = 123.24°$, $\alpha \approx 90°$, $\gamma \approx 90°$.[4)]

3. Experimental Procedure

NH_4HSO_4 is ordinarily obtained by slow evaporation of an aqueous solution of a stoichiometric mixture of $(NH_4)_2SO_4$ and H_2SO_4 at room temperature. The prepared crystals are transparent and colorless, and their dimensions are usually $5 \times 4 \times 4\,\mathrm{mm}^3$.

The nuclear magnetic resonance signals from the ^1H in NH_4HSO_4 were measured using a pulsed 200 MHz NMR spectrometer at the Korea Basic Science Institute. The static magnetic field was 4.7 T, and the central rf frequency was set at $\omega_o/2\pi = 200$ MHz for the ^1H nucleus. The ^1H NMR spectra were taken using a solid echo pulse sequence, $(\pi/2_x - \tau - \pi/2_y)$, to eliminate artifacts due to probe ringing. The width of the $\pi/2$ pulse used was 5 μs, and the pulse separation τ was 40 μs. The sample temperature was maintained at a constant value by controlling the helium gas flow and the heater current, giving an accuracy of ±0.1 K.

4. Experimental Results and Analysis

Figure 2 shows the variation of the FWHM (full width at half maximum) of the ^1H line as a function of temperature. As the temperature is lowered, the line width increases in a step-like shape, reaching a rigid lattice value at lower temperatures. This stepwise narrowing is generally considered to be caused by internal motions which have a temperature-dependence connected with that observed for the line width.[18)] In the transition region between 160 K and 270 K, the shape of the line changes, going progressively from the Gaussian-like shape of a rigid lattice to a Lorentzian shape. For temperatures above 270 K, a very considerable narrowing of the line occurs, and it has nearly a Lorentzian shape.

The proton spin-lattice relaxation time was measured in the temperature range of 120 K to 300 K at a frequency of 200 MHz. The spin-lattice relaxation recovery patterns can be quite well described with a single exponential at all temperatures. The values of T_1 measured below 300 K are given as a function of $1000/T$ in Fig. 3. The change in the curve of T_1 near 160 K corresponds to the phase transition, although the line width is unchanged. However, the other phase transition (= 270 K) cannot be distinguished from the NMR results. The variation of T_1 with temperature exhibits a minimum of 289 ms at 202 K. This result is consistent with the trend of T_1 for the ^1H nucleus in $NH_4H_2PO_4$ and NH_4SCN single crystals.[19–21)] This feature of T_1 indicates that distinct molecular motion is present. The T_1 in phase I below 160 K corresponds to slow motion. In phase III above 270 K, the relaxation time increases with increasing temperature, corresponding to fast motion. In phase II, the form of the proton T_1 vs. inverse temperature curve leads us to believe that the relaxation process is caused by the NH_4^+ motion. However, the calculated T_1 (minimum) value of 38.8 ms is much lower than the observed value of 289 ms, the depth of the minimum being determined by the magnitude of the second moment modulated by the variation of the N–H dipolar interaction.

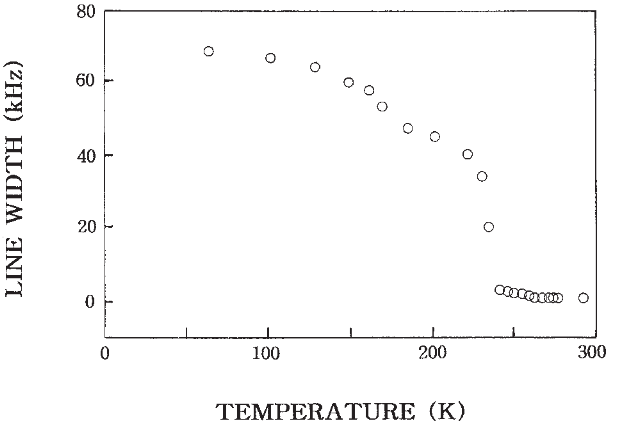

Fig. 2. ^1H NMR line width as a function of temperature.

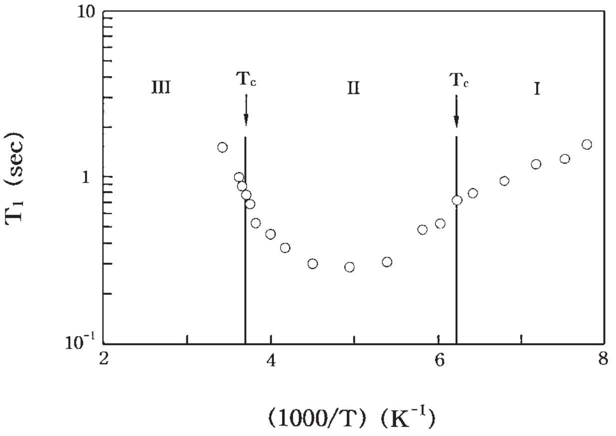

Fig. 3. Temperature dependence of the spin-lattice relaxation time, T_1, for ^1H in a NH_4HSO_4 single crystal.

In studies of molecular motion in relation to the experimental relaxation time, it is important to know whether the relaxation time is located on the slow side of the minimum or on the fast side of the minimum as a function of the inverse temperature. Also, the T_1 values can be related to corresponding values of the rotational correlation time, τ_c, the rotational correlation time being the length of time that a molecule remains in a given state before the molecule reorients. As such, τ_c is a direct measure of the rate of motion. For spin-lattice relaxation times, the experimental value of T_1 can be expressed in terms of an isotropic correlation time τ_c for molecular motions by using the Bloembergen–Purcell–Pound (BPP) function:[18,22)]

$$T_1^{-1} = 9/10(\gamma^2\hbar/r^3)^2[\tau_c/(1+\omega_o^2\tau_c^2) + 4\tau_c/(1+4\omega_o^2\tau_c^2)] \tag{1}$$

Here, γ represents the gyromagnetic ratios for the ^1H nucleus, r is the proton–proton separation, 1.68 Å for the NH_4 ion, $\hbar = h/2\pi$ where h is the Planck's constant, and ω_o represents the proton Larmor frequencies. The minima occur when the NH_4 ions have $\omega_o\tau_c = 0.616$. The BPP relation

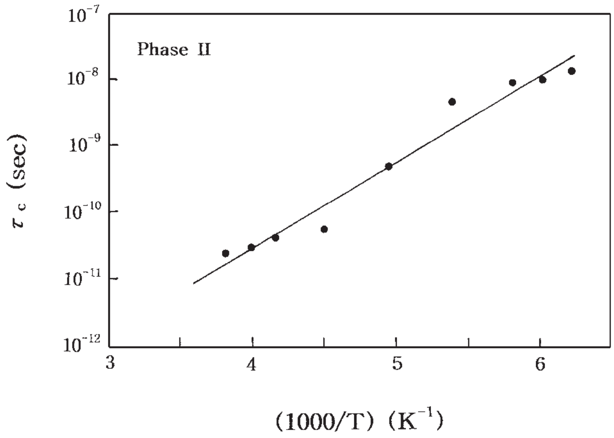

Fig. 4. Arrhenius plot of the natural logarithm of the correlation times in phase II for the proton as a function of the inverse temperature.

between T_1 and the characteristic frequency of motion ω_o can be applied. Since the T_1 curves were found to exhibit a minimum, it was possible to determine the constant in the BPP formula. We were then able to calculate the parameter τ_c as a function of temperature, as shown in Fig. 4.

The temperature dependence of τ_c follows a simple Arrhenius expression:[22,23]

$$\tau_c = \tau_o \exp(E_a/RT), \tag{2}$$

and, the slopes of the straight line portions of the semilog plots determine the values for the activation energy, E_a. The activation energies for the reorientational motions in phases I and III can be obtained from portions of the $\log T_1$ vs. $1000/T$ curve. Those energies were 0.98 and 4.61 kcal/mol, respectively. Also, we calculated the activation energy for NH_4^+ molecular motion in phase II to be 5.92 kcal/mol.

5. Discussion and Conclusions

The proton NMR line width and spin-lattice relaxation times were studied for NH_4HSO_4 between 120 and 300 K. The changes in the proton relaxation behavior in the neighborhood of the phase transition temperature indicate a change in the state of the internal motion at the transition. In simple NMR theory, the general behavior of the spin-lattice relaxation time for random motions of an Arrhenius type with a correlation time τ_c is described in terms of two regions: fast and slow motion. For the fast motion region, i.e., for, $\omega_o\tau_c \ll 1$, $T_1^{-1} \sim \exp[E_a/RT]$, and for the slow motion region, i.e., for $\omega_o\tau_c \gg 1$, $T_1^{-1} \sim \omega_o^{-2}\exp[-E_a/RT]$. The motions in phases I and III undergo reorientational motion whereas the T_1 minimum in phase II is attributed to the molecular motion of the NH_4 group. The large change in the activation energy between phases I and II indicates that the NH_4 groups are affected during this transition, while the motions of the NH_4^+ ions between phases II and III not playing an important role in the phase change. These results are consistent with those reported for several experimental method.[11,12,14] According to Miller *et al.*,[13] the ^1H spin-lattice relaxation time shows a large change at 173 K instead of 160 K. However, the T_1 for the ^1H in the NH_4HSO_4 crystals used here was well defined by the BPP theory, and the proton T_1 showed no sudden changes near 173 K. Consequently, NH_4HSO_4 single crystals may have different properties, depending on the crystal growth conditions.

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1) M. M. Abdel-Kader, A. El-Shawarby, W. M. Housny, Z. H. El-Tanahy and F. El-Kabbany: Mater. Res. Bull. **29** (1994) 317.
2) A. R. Lim, D. Y. Jeong and S. Y. Jeong: J. Phys.: Condens. Matter **13** (2001) 3511.
3) A. R. Lim, J. K. Jung and H. M. Park: J. Phys. Soc. Jpn. **70** (2001) 3708.
4) R. Pepinsky, K. Vedam, S. Hoshino and Y. Okaya: Phys. Rev. **111** (1958) 1508.
5) R. Pepinsky and K. Vedam: Phys. Rev. **117** (1960) 1502.
6) D. Kh. Blat and V. I. Zinenko: Sov. Phys. Solid State **18** (1976) 2096.
7) B. A. Strukov, V. A. Koptsik and V. D. Ligasova: Sov. Phys. Solid State **4** (1962) 977.
8) D. K. Blat and V. I. Zinenko: Sov. Phys. Solid State **18** (1976) 2096.
9) T. Kondo, Y. Ishibashi and Y. Takagi: J. Phys. Soc. Jpn. **37** (1974) 1708.
10) T. Kondo, Y. Ishibashi and Y. Takagi: J. Phys. Soc. Jpn. **39** (1975) 1326.
11) P. A. Bazhulin, T. P. Myasnikova and A. V. Rakov: Sov. Phys. Solid State **5** (1963) 1299.
12) T. P. Myasnikova and A. F. Yatsenko: Sov. Phys. Solid State **4** (1962) 475.
13) S. R. Miller, R. Blinc, M. Brenman and J. S. Waugh: Phys. Rev. **126** (1962) 528.
14) J. J. Rush and T. I. Taylor: *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1965) Vol. II, p. 333.
15) A. R. Lim, J. K. Jung and S. Y. Jeong: Solid State Commun. **118** (2001) 453.
16) R. J. Nelmes: Acta Cryst. B **27** (1971) 272.
17) R. J. Nelmes: Ferroelectrics **4** (1972) 133.
18) N. Bloembergen, E. M. Purcell and R. V. Pound: Phys. Rev. **73** (1948) 679.
19) R. Ikeda and C. A. McDowell: Mol. Phys. **25** (1973) 1217.
20) J. A. Ripmeester and N. S. Dalal: Phys. Rev. B **18** (1978) 3739.
21) N. S. Dalal, C. A. McDowell and R. Srinivasan: J. Chem. Phys. **60** (1974) 3787.
22) A. Abragam: *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1989).
23) B. Cowan: *Nuclear Magnetic Resonance and Relaxation* (Cambridge University Press, Cambridge, 1997).